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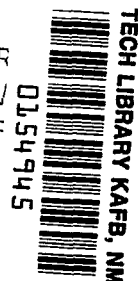
VACANCY FORMATION IN GOLD UNDER HIGH PRESSURE

by Hubert H. Grimes

Lewis Research Center

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

High-purity gold wires were resistively heated and quenched in a pure argon gas environment at pressures up to 6 kilobars. Quench rates of 10^4 to 5×10^4 °C per second were obtained by abruptly reducing the heating current. The resistance of both the specimen and an unquenched dummy specimen were measured at -38° C with conventional circuits. The logarithm of the quenched-in resistance decreased linearly with increasing pressure at a constant temperature of 600° C. From these data, a formation volume of 0.52±0.07 atomic volume was derived, which was assumed to be associated with the formation of single vacancies. For atmospheric pressure quenches from below 725° C, Arrhenius plots of the quenched-in resistivity for various quenching temperatures yielded an average formation energy for single vacancies of 0.93 electron volt. Above 725° C, the quenched-in resistivity drops below this line consistent with the complex annealing behavior during the quench observed by others for higher temperature quenches. The measured formation volume indicated a degree of relaxation around a vacancy that is shown to be in accord with previously calculated lattice relaxations obtained using potential function theory.

INTRODUCTION

Large elastic strains have been shown to have a significant effect on self-diffusion in several metals (refs. 1 to 5). Compressive strains resulting from the application of hydrostatic pressures of 5 to 10 kilobars have reduced the diffusion coefficient by as much as an order of magnitude. Theory predicts that the principal manifestation of the strain arises in the exponential part of the diffusion equation associated with the energy required to form a vacancy in the deformed crystal and with the energy an atom requires to surmount a potential barrier along the diffusion path (ref. 6). But this theory does not make it possible to predict a priori the relative importance of these two effects. However, several quenching and annealing experiments on the noble metals have resulted in the independent determination of the formation energy and migration energy of vacancies in unstrained materials. These techniques have been extended to strained systems for vacancy annealing in gold (ref. 7), and at the time of this writing, for quenching in gold (informa-

tion received in a private communication with R. P. Huebener and C. G. Homan). Other methods, the change in macroscopic length (ref. 8) and the calorimetric measurement of the energy stored in a quenched crystal (ref. 9), have been used to determine, indirectly, the effect of strain on vacancy formation.

The technique reported herein is the most direct; it involves determination of the vacancy concentration by a measurement of the excess electrical resistivity quenched into gold wires that are subjected to large hydrostatic pressures. The data permit the calculation of not only the energy of formation of the vacancy but also the volume change of the crystal accompanying the formation of a vacancy. The volume obtained indicates the degree of relaxation of the lattice atoms around the vacancy. This relaxation is compared with calculated estimates of this quantity obtained using simple pairwise potential function theory (ref. 10).

THEORY

It has been shown that by rapidly quenching fine metal wires from elevated temperature to room temperature or below, a large fraction of the point defects, in equilibrium with the crystal lattice at the high temperature, can be retained (ref. 8). The measure of this defect supersaturation at the low temperature is reflected in an increase in the electrical resistivity of the wire. Annealing of these defects in gold has indicated that defects quenched from below 700° C, at quench rates of 10^3 to 10^5 $^{\circ}$C per second or more, are predominately single vacancies. Above this temperature, more complex defect annealing occurs and has been the subject of several theoretical and experimental studies (refs. 11 to 13). For simplicity of interpretation, therefore, the quenches under high pressures in this study were done at 600° C.

The number of vacancies n_V, which are in equilibrium with a crystal lattice at absolute temperature T, can be expressed as

$$n_V = Ne^{-\Delta G_f/kT} \tag{1}$$

where N is the total number of possible lattice sites at which a vacancy can exist and ΔG_f is the change in the Gibbs free energy of the crystal accompanying the formation of a vacancy. Using the thermodynamic relation that the Gibbs free energy is related to the formation energy ΔH_f, or enthalpy, and to the entropy of formation ΔS_f by the expression

$$\Delta G_f = \Delta H_f - T \Delta S_f \tag{2}$$

and also using the observation that the fractional vacancy concentration quenched into a crystal from a temperature T_Q at pressure p is proportional to the resistivity increase $\Delta \rho_V$ on quenching, gives, for the quenched-in resistivity,

$$\Delta\rho_V = A\,\frac{n_v}{N} = Ae^{-\Delta G_f/kT_Q} = Ae^{\Delta S_f/k}\,e^{-\Delta H_f/kT_Q} \qquad (3)$$

where A is a constant independent of temperature and pressure. It follows from equation (3) that $\ln \Delta\rho_V$ is linear in $1/T_Q$ with a slope

$$\sum = \frac{\delta(\ln \Delta\rho_V)}{\delta \frac{1}{T_Q}} = -\frac{\Delta G_f}{k} = -\frac{\Delta H_f}{k}$$

if ΔS_f is also assumed to be independent of temperature. This last assumption has been justified experimentally, and the energy of formation of a vacancy may be derived from the slope of such a curve.

At constant temperature the derivative of the Gibbs free energy with pressure is a volume, which for ΔG_f has the interpretation of the volume change a crystal experiences on formation of a vacancy. This derivative, from use of equation (3), is

$$\left(\frac{\partial \Delta G_f}{\partial p}\right)_T = \Delta V_f = -kT_Q\left[\frac{\partial(\ln \Delta\rho_V)}{\partial p}\right]_T \qquad (4)$$

Accordingly, the formation volume can be determined from a plot of $\ln \Delta\rho_V$ against pressure for quenches from a constant temperature.

EXPERIMENT

The large hydrostatic pressures required in this experiment were obtained with a three-stage gas pumping system capable of attaining pressures up to 13 kilobars in a cylindrical vessel with internal dimensions of 2 inches in diameter and 8 inches high. High-purity argon gas (99.995 percent) was used as the high-pressure fluid because it is chemically inert and has favorable thermodynamic properties. Gas chromatographic analysis of the argon confirmed the listed purity. The pressure system was operated with a minimum of lubrication to avoid thermal decomposition of oil on the specimen at elevated temperatures. The high pressures were measured with a calibrated Manganin gage, linear to within 1 percent in the pressure range used.

The specimen holder used for both the high- and low-pressure quenches is shown in figure 1. It is essentially an aluminum housing that encloses horizontally suspended specimen and dummy specimen wires. This enclosure is supported in good thermal contact with a 7/8 inch (O.D.), 1/4 inch (I.D.) steel tube that is closed on the lower end. Ethanol cooled to dry-ice - ethanol bath temperature was circulated through this steel "cold thimble" through a specially designed pressure vessel closure. In this way it was possible to cool the specimen enclosure even when the vessel was at high pressure.

The specimen enclosure was built up in sections to facilitate the insertion and suspension of the specimen and dummy specimen and the mounting of thermocouples. In the finished construction the specimen and dummy specimen wires
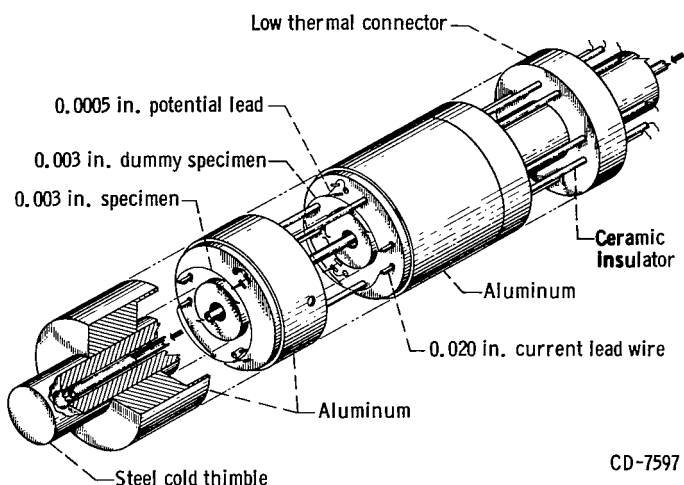

Figure 1. - Exploded drawing of specimen enclosure and cold thimble showing arrangement of specimen and dummy specimen wires.

remained suspended at the center of individual 1/4-inch cross-sectional annular cavities surrounding the cold thimble. With this arrangement, the temperature of the wires could be precisely maintained near -38° C by heat exchange with the cold walls of the cavities. The enclosure was provided with small baffled vent holes to permit passage of the high pressure gas. The entire specimen holder assembly was surrounded with a Lucite jacket that both insulated the cold assembly from the pressure vessel wall and reduced the dead space in the vessel.

A conventional circuit (ref. 14), shown schematically in figure 2, was used in the measurement of the quenched-in resistance. A differential measuring technique, used to improve
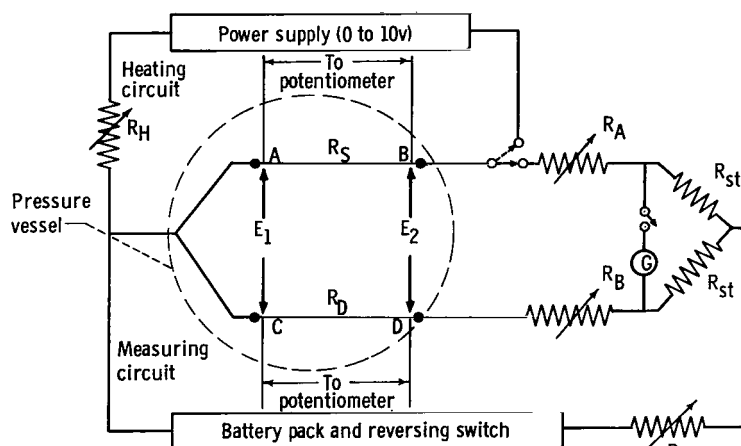

Figure 2. - Schematic diagram of circuit used for resistance measurements.

sensitivity, compared the resistance of the quenched specimen to an unquenched dummy specimen. The dummy specimen also served to compensate for ambient temperature changes of the assembly before and after the quench.

To make a measurement, the bridge circuit, including the specimen R_S, the dummy R_D, and two 1-ohm standard resistors R_{st}, was balanced by adjusting the variable resistors R_A and R_B. In the balanced bridge, the measuring currents in the specimen and

the dummy could be maintained equal to 1 part in 100,000. The resistance difference between the specimen and the dummy specimen was then determined by measurement of the potential differences E_1 and E_2 with a modified White potentiometer accurate to 10^{-8} volt. Errors due to constant thermal electromotive forces were eliminated by reversing the measuring current flow in the circuit. The resistance difference was then given by

4

$$R_S - R_D = \frac{E_1 - E_2}{I}$$

where E_1 and E_2 are averages of the forward and reverse readings. The measuring current I (nominally 10 ma in each arm of the bridge) was determined by measuring the potential drop across one of the 1-ohm standard resistors. This value of measuring current was found to minimize heating of the specimen and the dummy specimen, while permitting the quenched-in resistance to be determined to within 1 percent of the total value for most quenches.

The specimens and dummy specimens were, in all cases, fabricated from 0.003-inch-diameter gold wire from the same lot, quoted by the supplier as better than 99.999 percent pure. Resistivity ratios of 1400, for annealed specimens at room temperature and 4.2° K, confirmed this purity.

The physical arrangement of the specimen and the dummy specimen are shown in figure 1. They are supported in a horizontal position by fine 0.0005-inch-diameter gold wire hangers, two of which serve as potential leads. The specimen length defined by the potential leads was nominally 2 centimeters for most specimens. The dummy specimen length was matched potentiometrically to the specimen to reduce errors due to ambient temperature changes in the whole assembly. The success of this matching procedure was indicated by the agreement of the quenching results from these specimens with other specimens 7 centimeters long and similarly matched.

During the prequench anneal it was important to keep a reasonably uniform temperature over the test section of the specimen. In a series of preliminary experiments with the system just described, the temperature distribution along the test length was found to remain constant within 5° C at the quench temperature. This was determined by both optical pyrometry at atmospheric pressure and by thermocouple measurements at high pressures. Since no serious temperature fluctuations occurred along the specimens at high pressures, subsequent quench temperatures were measured by resistivity changes of the specimen. The proportionality between resistance and resistivity (i.e., length to cross section ratio) was determined for each specimen by comparison of the specimen resistance measured at a known room temperature with the resistivity data of reference 15 for that temperature. The specimen temperature was continuously monitored during anneals using potentiometric strip-chart recorders. During the normal prequench anneal, small cyclic fluctuations in temperature of approximately $\pm 3^{\circ}$ C were observed at higher pressures. A reasonable estimate of the total probable error in the measurement of the quench temperature is $\pm 5^{\circ}$ C.

Quench rates were measured as a function of pressure by an oscillographic technique. The specimen temperature was found to be nearly proportional to the potential drop across the specimen during most of the quench. The time rate of decay of this potential during the quench was observed on a calibrated persistent screen oscilloscope. From the quenching curves thus obtained, the initial quench rates (average slope over the first 100° C temperature drop) and the half-lives (time required to fall to one-half of the quench temperature) were recorded. A curve of half-life as a function of pressure (shown in

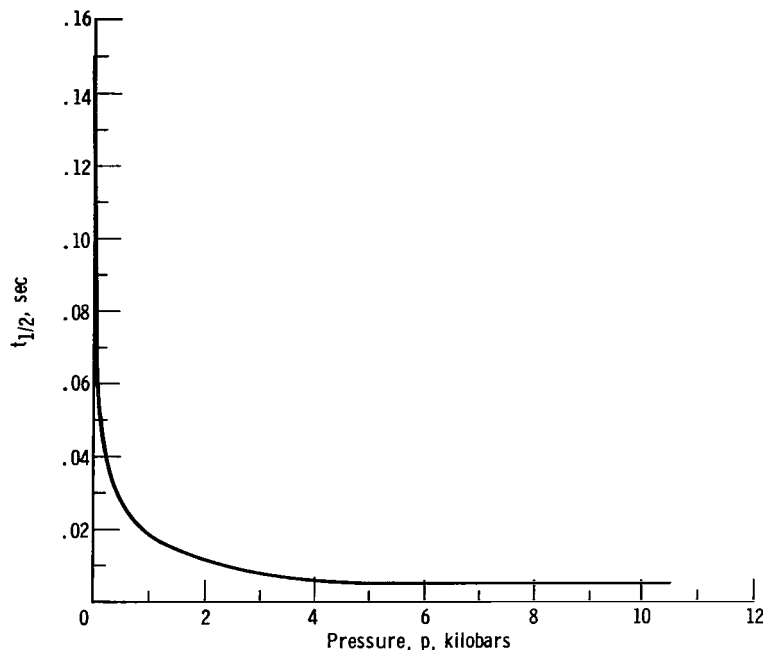fig. 3) illustrates the marked increase in quenching rate obtained at high pressures. It is significant, however, that the variation with pressure above about 1 kilobar is small. The half-life for the pressure runs in this study ranged from 2.5×10^{-2} to 5×10^{-3} second corresponding to initial rates of 10^4 to 5×10^4 $^\circ$C per second. It has been shown (ref. 16) that such a variation in quench rate for quenches below 600° C does not markedly affect the total quenched-in resistance of gold.

Figure 3. - Influence of pressure on time required for temperature of specimen wires to fall to one-half quenching temperature, 600° C ($t_{1/2}$).

The measurement procedure followed throughout most of the work reported herein was as follows.

Newly mounted specimens were given a high temperature anneal (temperatures from 800° to 900° C for 1 hr) followed by a gradual cooling to room temperature. Resistivity measurements at room temperature after subsequent anneals indicated no additional resistivity change after the first anneal. The sample holder was then cooled in the pressure vessel to the measuring temperature and, if desired, pressure was applied. Potentiometric measurement of resistance difference between the specimen and the dummy (R_S - R_D) was made with the balanced bridge circuit previously described. Several series of measurements were made over a period of time to determine whether the equilibrium measuring temperature was reached. Generally about five such consecutive resistance differences, constant to within ±1 microhm, established this. The specimen alone was then quickly heated to the quench temperature, held there for about 3 to 5 seconds (sufficient to establish the equilibrium vacancy concentration (ref. 17), and then quenched by turning off the heating current. The value of the resistance difference was again measured after the system returned to equilibrium as before, once more with the requirement of constancy of readings. The change in the resistance difference from the value obtained before the quench was then interpreted in terms of the excess vacancy concentration characteristic of the particular quench temperature and pressure used.

RESULTS

To determine the validity of the experimental techniques used, the addi-

tional resistance quenched into several specimens at atmospheric pressure was determined as a function of quenching temperature. From equation (3) it follows that from the slope of a plot of log $(\Delta R/R)$ against $1/T$, the formation energy for the defect may be obtained. Figure 4 shows the fractional resistance quenched into three specimens in the temperature range from $510°$ to $890°$ C. The curves shown are displaced vertically for the sake of clarity. The curves for specimens A and B actually involved the use of the same wire but with a slightly different heat treatment prior to quench. The data from these curves, as well as those for specimen C, actually superimpose, indicating the effectiveness of the annealing procedures. Some curvature is seen in the temperature region above $725°$ C, indicating that annealing is occurring during quenches from above this temperature. The observed linearity below this temperature supports the assumption that simple defect production predominates. The best fit of the data below $725°$ C gives formation energies of 0.90, 0.93, and 0.97 electron volt. The average of these three determinations is 0.93 electron volt.
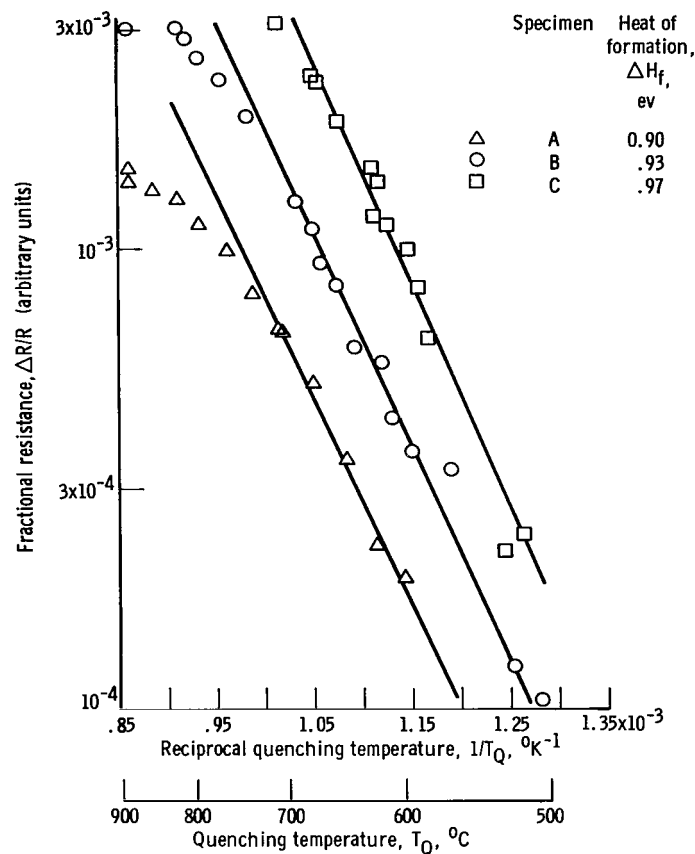

Figure 4. – Semilogarithmic plot of quenched-in resistance as a function of reciprocal of absolute quenching temperature at atmospheric pressure. (Curves for three specimens are displaced vertically for the sake of clarity.)

The results obtained from quenches made under high pressures are given in table I. The quenched-in resistance was corrected to $600°$ C by use of an Arrhenius type equation using the value of 0.93 electron volt for the formation energy and the assumption that the change of the derivative of the energy with pressure is temperature independent over the small temperature interval in which the data were obtained.

A semilogarithmic plot of the corrected resistivities as functions of pressure is shown in figure 5. The slope of the curve of figure 5 in equation (4) yields a formation volume of ΔV_f of 5.45 ± 0.7 cubic centimeters per mole. The molar volume of gold at $600°$ C can be estimated from the molar volume at room temperature, the thermal expansion, and the compressibility.

7

The value obtained is 10.45 cubic centimeters per mole. The specific change per defect is then

$$\frac{5.45 \ cm^3/mole}{10.45 \ cm^3/mole} = 0.52\pm0.07 \ at. \ vol.$$

TABLE I. - DATA FOR PRESSURE RUNS

Pressure, p, bars	Quenching temperature, T_Q °C	Fractional resistance, $\Delta R/R$ (a)	Corrected fractional resistance, $(\Delta R/R)_{corr}$ (b)
0	509	1.60×10^{-4}	8.53×10^{-4}
783	592	7.35	8.16
2300	612	8.88	7.50
2550	590	6.17	7.18
3050	598	6.68	6.88
3720	570	4.24	6.60
3800	584	5.17	6.48
4600	579	4.42	6.15
5360	591	5.44	6.03
6100	581	4.22	5.60

[a]Fractional resistance quenched into several specimens at quenching temperature T_Q.
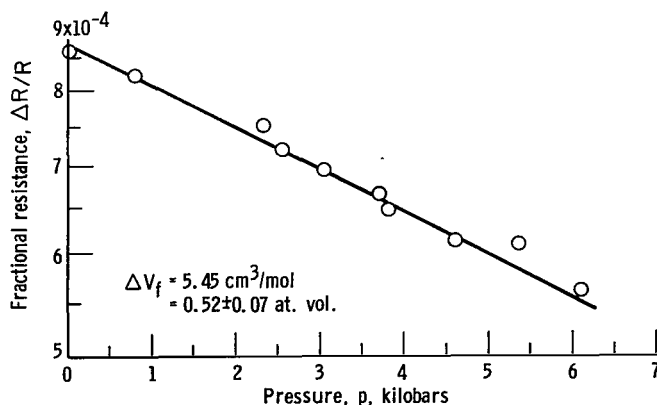
[b]Fractional resistance corrected to 600° C.

Figure 5. - Influence of pressure on fractional resistance retained in gold wires quenched from 600° C.

$\Delta V_f = 5.45 \ cm^3/mol$
$= 0.52\pm0.07 \ at. \ vol.$

DISCUSSION

Formation Energy

The energy for defect formation obtained from figure 4 is in good agreement with the values, quite generally accepted as the single vacancy formation energy, obtained from atmospheric quenching experiments and from calorimetric, dilametric, and other methods. The best estimates from these measurements range from 0.94 to 0.98 electron volt (ref. 18). Above about 725° C, deviations from linearity appear in the curves of figure 4 possibly indicating annealing during the quenches from above this temperature. This deviation is consistent with the quenching studies of reference 16 for the quench rates obtainable at atmospheric pressure in this experiment. The agreement of the formation energy calculated from the lower temperature data with the existing best estimates engenders confidence in these techniques. This confidence is extended to the results from the high pressure quenches performed at variable but higher quench rates.

Formation Volume

The value obtained for the formation volume is in good agreement with the value of 0.53 atomic volume (private communication with R. P. Huebener and C. G. Homan) obtained

by high-pressure quenching. It is also in agreement with the value of 0.57 atomic volume from reference 9, where ΔV_f was derived indirectly by combination of the vacancy formation energy and the value of the vacancy concentration obtained from the energy released on annealing vacancies in gold foils with the resistivity change of gold wires per fractional volume change measured by the investigators of reference 8.

Calculated estimates from reference 19 for the vacancy formation volume in copper ranging from 0.47 to 0.55 atomic volume are also in agreement with the measured value.

A theoretical estimate of the degree of relaxation of nearest neighbor atoms to the vacancy can be made assuming the Eshelby elastic continuum approximation (ref. 20). For face-centered-cubic metals, the relaxation δ is given by

$$\delta = \frac{V_f}{12\pi\sqrt{2}\left(\dfrac{1 - \sigma}{1 + \sigma}\right)}$$

where V_f is the measured formation volume and σ is Poisson's ratio.

Poisson's ratio of 0.42 for gold (ref. 21) and the measured formation volume of 0.52 atomic volume give the inward relaxation of nearest neighbors to the vacancy as 2.4 percent. This value compares favorably with a relaxation of 2.24 percent for copper calculated with a Morse potential function (ref. 10). This remarkable agreement tends to justify the validity of the use of a simple pairwise potential function for lattice calculations in which drastic atomic rearrangement does not occur.

The measured formation volume, when added to the vacancy migration volume for gold from reference 7, yields an activation volume for self-diffusion in gold of 0.67 atomic volume. This value may be compared with 0.7 atomic volume measured for self-diffusion in lead (ref. 4) and 0.9 atomic volume reported for self-diffusion in silver (ref. 5). To the author's knowledge, the activation volume for self-diffusion in gold has not been measured; however, because both the formation volume and the migration volume have been measured, a direct comparison with the diffusion volume would be most interesting.

Finally, the resistivity change of gold wires accompanying a fractional volume change $\Delta_\rho/(\Delta V/V) = 3.2\times10^{-4}$ ohm-centimeter (ref. 8) and the fractional formation volume measured can be used to calculate the resistivity per atomic percent vacancies. The value obtained, 1.67 ohm-centimeter per atomic percent vacancies, is in fair to good agreement with several theoretical estimates for copper made since 1953 (ref. 22) ranging from 1.25 to the most recent value 1.67 ohm-centimeter per atomic percent vacancies.

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